

Page 12, line 26, change " $P > \frac{2\sqrt{3kTm}}{\tau} N_{ss}$ " to

$P > \frac{2\sqrt{3kTm}}{\tau} N_{ss}$

REMARKS

Applicants respectfully request entry of revised literal translation appended hereto.

I. CHANGES TO THE SUBSTITUTE SPECIFICATION

Claims 1-62 are pending. By this Supplemental Preliminary Amendment, the Substitute Specification is amended.

The changes are as follows:

A. On Page 1, line 37, " $10 \text{ cm}^{-2} \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ to $100 \text{ cm}^{-2} \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ " is changed to " $10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ to $100 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ ". This change is necessitated by an inadvertent clerical error in the literal translation whereby " cm^{-2} " was inadvertently provided instead of " cm^2 ". This error is also been corrected in the attached revised literal translation.

B. On Page 2, line 5-6, " $0.1 \text{ cm}^{-2} \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ to $1 \text{ cm}^{-2} \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ " was changed to " $0.1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ to $1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ ". This change is necessitated by an inadvertent clerical error in the literal translation whereby " cm^{-2} " was inadvertently provided instead of " cm^2 ". This error is also been corrected in the attached revised literal translation.

C. On Page 12, line 12, the equation " $F = \frac{1}{6} CV = \frac{1}{\sqrt{3kTm}}$ " is changed to " $F = \frac{1}{6} cv = \frac{1}{2\sqrt{3kTm}}$ ". This change is necessary to conform the substitute specification

with the literal translation. The "CV" is no longer capitalized and the "1/2" is added to the right side of the equation. This change conforms the Substitute Specification to the literal translation filed on September 30, 1997.

D. On page 12, line 26, the equation " $P > \frac{2\sqrt{3kTM}}{\tau} N_{ss}$ " is changed to " $P > \frac{2\sqrt{3kTm}}{\tau} N_{ss}$ ". This change corrects the inadvertent capitalized "M" and changes it to a small "m" in conformance with the literal translation filed on September 30, 1997.

II. CHANGES TO THE LITERAL TRANSLATION

A revised literal translation is attached as a substitute for the literal translation filed September 30, 1997. The revised literal translation includes the following revisions which correct typographical errors. The correction of these typographical errors does not raise new matter because the changes are supported by the corresponding Japanese language PCT Application, i.e., PCT/JP97/00213. The literal translation filed September 30 is amended as follows:

A. Page 2, line 14, same change as indicated in Section IA of this Supplemental Preliminary Amendment.

B. Page 2, lines 18-19, same change as indicated in Section IA of this Supplemental Preliminary Amendment.

C. Page 18, line 6, "(m-3)" should read " (m^{-3}) ".

D. On page 18, line 9, line 1

$$F = \frac{1}{6} cv = \frac{1}{2} \sqrt{3kTm}$$

should read:

$$F = \frac{1}{6} cv = \frac{1}{2} \frac{1}{\sqrt{3kTm}} .$$

E. On page 19,

$$2 \sqrt{3kTm}$$

$$P > Nss$$

τ

should read:


$$P > \frac{2\sqrt{3kTm}}{\tau} N_{ss} .$$

III. Conclusion

Applicants respectfully request entry of the above amendments to the Substitute Specification and entry of the attached revised literal translation. The amendments and changes to the literal translation correct clerical and typographical errors. No new matter has been introduced

because the changes are all supported by the Japanese language
PCT Application.

Respectfully submitted,



James A. Oliff
Registration No. 27,075

Eric D. Morehouse
Registration No. 38,565

JAO:AJV/clh

OLIFF & BERRIDGE
P.O. Box 19928
Alexandria, Virginia 22320
Telephone: (703) 836-6400

~~SPECIFICATION~~

HIGH ENERGY SUPPLY APPARATUS, METHOD OF FORMING CRYSTALLINE FILM AND METHOD OF MANUFACTURING THIN FILM ELECTRONIC DEVICE

BACKGROUND OF THE INVENTION

1. ~~Technical Field~~ Field of ^{the} Invention

The ~~present~~ invention relates to a high energy supply apparatus such as a laser irradiation apparatus ~~as a~~ ~~representative,~~ a method of forming a crystalline film by using the high energy supply device, and a method of manufacturing a thin film electronic device ~~comprising the~~ ^{including a} crystalline film formed by the method.

2. ~~Background Art~~ Description of Related Art

As ~~the~~ screen size and ~~resolution~~ of a liquid crystal display (LCD) ^{resolution LCD} increase, ~~a driving system therefor is~~ are transferred from a simple matrix system to an active matrix system, ^{the} thereby enabling display of large volumes of information. The active matrix system ^{enable} permits LCD devices ^{to have more than} having over several hundreds of thousands of pixels and ~~which includes~~ These systems include ~~comprises a~~ switching element, such as a thin film transistor (TFT), for each pixel. As substrates for ~~various types of LCD,~~ Transparent insulating substrates, such as a fused quartz plate, a glass plate, ~~and the like~~

which enable transmission type displays are used. As an ^{as substrates for various types of LCD devices}
~~active layer of such a TFT~~ ^A semiconductor film of
 amorphous silicon (a-Si) ^{or} polycrystalline silicon (poly-Si) ^{to form an active layer for the TFT.} ~~or the like~~ is generally used. ~~When not only the both~~
^{and the} pixel switching element ~~but also a~~ driving circuit are
 integrally formed ~~by~~ using ^a TFT, it is necessary and
 essential to use polycrystalline silicon exhibiting a high
 operation speed. ^{When a} ~~In use of the~~ polycrystalline silicon
^{is utilized} film ^{the} as the active layer, ^a TFT is generally formed by using
 a fused quartz plate as a substrate in a manufacturing
 method referred to as a high-temperature ~~process~~ ^{process} in which
 the ~~highest~~ ^{maximum} temperature ~~of the process~~ exceeds 1000°C. In
 this case, the mobility of the polycrystalline silicon
 film is ~~about~~ ^{approximately} $10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ to $100 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. On the other
^{when} hand, ~~in use of~~ an amorphous silicon ^{is utilized to form} as the active layer,
 the highest temperature of the process is as low as ~~about~~ ^{approximately}
 400°C, and a glass substrate is thus generally used. The
 mobility of the amorphous silicon film is ~~about~~ ^{approximately} $0.1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ to $1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$.

Advances in enlargement of LCD display screens and
 reduction ⁱⁿ ~~of the~~ cost require the use of a low-cost glass
 plate as an insulating substrate. However, as described
 above, ~~the~~ amorphous silicon film is significantly
 inferior to ~~the~~ polycrystalline silicon film in electrical

~~properties, and has problems of a low operation speed. ~~For example,~~~~
 etc. On the other hand, the polycrystalline silicon TFT
 produced by the high temperature process ^{includes} ~~comprises~~ a fused
 quartz plate, and thus ^{is subject to the problem of increasing} ~~has the problems of causing~~
~~difficulties in enlarging a LCD and reducing the cost~~
~~thereof.~~ Therefore, there is strong demand for a
 technique for forming a thin film semiconductor device
^{which includes} ~~comprising~~ a crystalline semiconductor film, such as a
 polycrystalline silicon film, ~~or the like~~ as an active
 layer formed on a usual glass substrate. ^{In the case of a} In use of a
^{conventional} ~~A usual~~ large glass substrate ^{which has a} ~~having~~ high mass productivity,
^{approximately} the highest temperature of the process is limited to about
 400°C or less in order to avoid deformation of the
 substrate. This is referred to as a "low-temperature
 process poly-Si TFT" and ^{is} ~~now~~ under development.
~~Eventually,~~ ^{for development of a} The most important technical problem ~~of the~~
 low-temperature process poly-Si TFT lies in ~~how to form an~~ ^{ing}
 an excellent crystalline film ^{utilizing} ~~by~~ a processing temperature of
 400°C or less, i.e., how to improve an apparatus for
 forming a good crystalline film. ^{Solving the aforementioned difficulties} ~~Solution to such a~~
~~problem~~ ^{development of} enables not only the formation of a good TFT and ~~a~~
^{and} LCD ~~comprising this TFT but~~ also significant ^s ~~improvements~~
^{the} ~~in~~ performance of all electronic devices, such as solar
 cells and semiconductor device circuits, which are formed

by using crystalline films. At the same time, this enables a further reduction of the cost.

Conventionally, as First prior art is disclosed in SID (Society for Information Display) '93 Digest P. 387 (1993), in which a crystalline film is formed at a low temperature, and a thin film electronic device comprising the film is formed. In this prior art, A polycrystalline silicon film is formed as the crystalline film, and a TFT is formed as the thin film electronic device. The crystalline film is formed by depositing an a-Si film of 50 nm by a low-pressure chemical vapor phase deposition process (LPCVD process) using monosilane (SiH_4) as a raw material at a deposition temperature of 550°C, and then applying a laser beam to the thus formed a-Si film. Although not disclosed in this digest, irradiation of the laser beam is carried out by the laser irradiation apparatus 101 shown in Fig. 1. The laser irradiation apparatus 101 includes a laser light emission source 102 and a laser irradiation chamber, a substrate having a material 103 to be irradiated such as the a-Si film which is placed on the surface thereof being disposed on a stage 105 provided in the laser irradiation chamber. In the laser irradiation chamber is provided a laser incident window comprising quartz glass or the like at a position opposite to the stage so that a laser beam

107 is incident through the laser incident window 106. The distance between the laser incident window and the substrate 104 is generally ~~about~~ ^{approximately} 1 cm. The material to be irradiated is irradiated with a laser beam at a stage temperature ~~at~~ ^{from} room temperature to about 400°C under vacuum pressure ~~of vacuum~~ to atmospheric pressure.

After the poly-Si film ~~comprising~~ ^{including} a crystalline film is obtained as described above, the thin film electronic device (TFT) is formed ~~by using~~ ^{utilizing} the poly-Si film. Specifically, after the poly-Si film is processed to a desired shape, an oxide film ~~functioning~~ ^{which functions} as a gate insulating film is deposited by a PECVD process ~~or the like~~. A gate electrode is formed on the gate insulating film by using tantalum (Ta), and then a source and a drain for a transistor are formed ~~in~~ in a self alignment manner ~~by injecting~~ ^{implanting} donor or acceptor impurities into the polycrystalline silicon film using the gate electrode as a mask. Impurities are ~~injected~~ ^{implanted} by an ion doping method using a mass non-separation type ~~injection~~ ^{implantation} apparatus and phosphine (PH₃) and diborane (B₂H₆) as raw material gases which are diluted with hydrogen. The ions injected are activated at 300°C. The insulating layer is then deposited, and electrodes and wiring are formed by using indium tin oxide (ITO) and aluminum (Al) to complete a

TFT.

~~Second prior art~~ ^{Another conventional method} for obtaining a crystalline semiconductor film at a low temperature is disclosed in Japanese Patent Laid-Open No. 7-99321. ~~In this second prior art,~~ ^A an a-Si film is formed and then irradiated with a laser beam to obtain a crystalline film. Irradiation of the laser beam is carried out under ^{vacuum} ~~pressure of vacuum~~ or in an inert gas atmosphere. In fact, the same publication discloses ~~in paragraph [0009]~~ the following. "At least the surface layer of the semiconductor thin film formed on the substrate is melted and recrystallized under reduced pressure or in an inert gas atmosphere, and the substrate (1) having the melted and recrystallized semiconductor film formed thereon is transferred to the step of forming an insulating film on the melted and recrystallized semiconductor film while being maintained under reduced pressure or in an inert gas atmosphere." ~~In the second prior art,~~ ^A a TFT is formed by a manufacturing method similar to the ^{conventional method described above} ~~basically the same as the first prior art~~ using the ~~thus~~ obtained polycrystalline silicon film. Eventually, in the ^{conventional methods} ~~both prior arts,~~ a crystalline film is obtained by irradiating a silicon film with a laser beam using the laser irradiation device shown in Fig. 2 under ^{vacuum} ~~pressure of vacuum~~ to atmospheric pressure or in an inert gas

atmosphere.

However, the above-mentioned ^{ion} ~~conventional~~ ^{forementioned} methods ~~prior arts are~~ ^{have} ~~considered as having~~ the following problems:

~~Problem~~(1) Irradiation under atmospheric pressure causes contamination of the crystalline film with impurities, such as oxygen and nitrogen or dust. Particularly, when the crystalline film ~~comprises~~ ^{includes} a semiconductor or a metal, contamination with oxygen or dust ~~brings about~~ ^{creates} significant deterioration in the physical properties of the thin film formed;

~~Problem~~(2) ^{The} ~~A~~ gas frequently used in crystallization under an inert gas atmosphere is nitrogen. Since nitrogen ^{is} ~~has~~ ^{reactive with} high reactivity ~~to~~ semiconductors such as silicon ~~and~~ ^{with} ~~the like~~ and metals such as tantalum ~~and the like~~, a high-purity crystalline semiconductor film and crystalline metallic film cannot be obtained.

~~Problem~~(3) Irradiation under ^a vacuum necessitates that a laser irradiation chamber with high sealing performance is provided, and a large scale evacuation device such as a turbo-molecular pump is added to a laser irradiation apparatus. This ~~brings about an increase in~~ ^{which includes} the cost of a thin film electronic device ~~comprising~~ a crystalline thin film, and ~~a~~ decreases ~~the~~ productivity;

~~Problem~~(4) In melt crystallization, the component

elements of the melted material irradiated with a laser beam are invariably scattered or evaporated. This phenomenon is particularly ^{pronounced} ~~remarkable~~ in laser irradiation under vacuum because melting under ^a vacuum causes ^{the} ~~the~~ formation of a deposited film. As a result, a film of the material irradiated with a laser beam is formed on the laser incident window of the laser irradiation apparatus.

Fig. 1 shows a scattered molecule 108 in this state. Evaporation of the material 103 to be irradiated and the formation of a film on the laser incident window represent attenuation of the laser energy applied to the material to be irradiated at each time of laser irradiation. Namely, the ^{conventional methods} ~~prior arts~~ are incapable of obtaining a crystalline film having good characteristics and ^{instead possess} ~~cause~~ large variations in film quality;

~~Problem~~ (5) When high energy is supplied to the material to be irradiated by laser irradiation ~~or the like~~ to progress melt crystallization, as the ^{supplied} energy increases, the quality of the crystalline film ~~obtained~~ is improved. However, in ^{vacuum} irradiation ~~under vacuum~~, ^{the} problem described in ^{above} (4) ^{difficult} becomes significant as the supplied energy increases. This makes it ^{difficult} substantially impossible to increase the ^{for vacuum} supplied energy ~~in irradiation under vacuum~~ and improve the quality of the crystalline film obtained; and

~~Problem~~ (6) In laser irradiation under vacuum or in an inert gas atmosphere, at the end of melt crystallization by irradiation, ^{where} ~~at the time~~ the material to be irradiated with a laser beam is transferred from a solution state to a crystal solid state~~s~~, the surface is reconstructed to minimize the surface energy, and many chemically active unpaired bonding electrons remain on the surface. The reconstructed surface having unpaired bonding electrons has a structure completely different from that of the internal crystal, and thus ^{exhibits} ~~shows~~ an energy band diagram ^{significantly} ~~greatly~~ different from that of the internal crystal. ^{Many electronic} ~~In~~ ^{devices employ} ~~both cases of a semiconductor thin film and a metallic thin film,~~ ^{surfaces.} ~~many electronic devices employ the surfaces of these films.~~ For example, ~~in a~~ field effect transistors (FET) ^{includes} ~~comprising~~ a semiconductor thin film, ^{where} ~~an~~ inversion layer ^{is} formed on the surface of the semiconductor to control the transfer process of electrons and holes in the semiconductor. In metal wiring, of course, a current flows through the surface of the metallic thin film. In a device (for example, a mirror and a metal catalyst) which employs the optical properties or chemical properties of a thin film, the ^{device} characteristics ~~thereof~~ are determined by the surface. [#] If the important surface having unpaired bonding electrons is greatly different from the inside due

to reconstruction, the physical properties of the surface also greatly change (generally deteriorate). For example, in a FET ~~comprising~~ ^{that includes} a semiconductor thin film, the mobility in the inversion layer is decreased to several tens to several % of the mobility of the inside of the semiconductor according to the surface state. The same phenomenon is observed in a metallic thin film (for example, the electric conductivity of the metallic thin film changes). As described above, control of the surface plays an important part in obtaining a good crystalline film. However, in a conventional crystallization method, such control is not sufficiently ~~made~~ ^{obtained}, and thus an ~~excellent~~ ^{superior} crystalline film cannot be obtained. Further, the characteristics of the crystalline film greatly vary with variations in the state of the reconstructed surface at each ~~time of~~ melt crystallization.

Accordingly, the ~~present~~ ^{object of the} invention is ~~aimed at~~ ^{to} solving ~~the~~ ^e above problems, ~~and an object material of the~~ ^{therefor} invention is to provide a high energy supply apparatus such as a laser irradiation apparatus, ~~as a representative,~~ a method of forming a good crystalline film using the high energy supply apparatus at a relatively low temperature, and a method of manufacturing a thin film electronic device ~~comprising~~ ^{including forming} the crystalline film formed by the

SUMMARY OF THE INVENTION

disclosed
method.

~~Disclosure of the Invention~~

Summary of the Invention *CAP*

~~Control of atmosphere in melt crystallization)~~

first step of the

In the ~~present~~ *material* invention, thin films of a

semiconductor such as silicon and a metal such as tantalum

are deposited on various substrates, ~~in a first step~~ and in the

second step at least the surface layers of these thin films are

partially melted and then crystallized through a cooling

solidification process *(hereinafter* ~~abbreviated to~~ "melt

crystallization" ~~hereinafter~~) to form various crystalline

films, ~~in a subsequent second step~~ Substrates to which

~~and thin films~~ *are* the ~~present~~ invention can be applied *will be described in*

hereafter below detail in Chapter (2-1), and the thin films will be

~~discussed in Chapter (2-2)~~ *refer to* The Crystalline films ~~mean~~

films in a single crystal state, a polycrystal state or a

mixed crystal state wherein a crystal and an amorphous

material are mixed. Melt crystallization is achieved by

supplying high energy such as a laser beam to the thin

films. Possible forms of high energy include

electromagnetic waves such as light, X-rays, and gamma

rays; ~~as representatives~~; charged particle flows such as

proton rays, electron rays, ^{and} alpha rays, ~~and the like;~~ and
 neutral elementary particle rays such as neutron rays and
 neutral meson rays, ~~as representatives.~~ [†] The elementary
 particle rays ^{are advantageous because} ~~have the advantage that~~ high energy can
 simply be supplied to the thin films through strong or
 weak interaction. Even when the thin films have low
 electric conductivity, ~~the~~ neutral elementary particle
 flows containing electromagnetic waves (photon) do not
 apply unnecessary charges to the thin films and thus do not
 electrically damage the thin films during supply of high
 energy. ^{This is} ~~Particularly~~ ^{important} when the thin films are intrinsic or
 nearly intrinsic semiconductor films, ~~this is important~~
 because these thin films have low electric conductivity.
 The charged particle flows have the advantage [†] that they
 can easily be formed by generating a plasma ^a of atoms, and
 that the direction [†] of the charged particle flows can
 easily be controlled. In view of the ease of handling, ^{including}
~~such as~~ formation and direction control, ^{and} ~~or safety for~~
~~living bodies,~~ ^{the} an optimum form of high energy material
 is electromagnetic waves with a wavelength ^{from} ~~of~~ about 10 nm to
 about 10 μ m, i.e., ~~so-called~~ light. Light can be
 classified ⁱⁿ to laser beams and nonlaser beams, both of which
 can be used as forms of high energy.

In the second step, metal crystallization proceeds in

a mixed gaseous
~~an atmosphere containing hydrogen such as a mixed gas~~
~~containing hydrogen molecules (H_2) and an inert gas; a~~
~~mixed gas containing a hydrogen halide such as hydrogen~~
~~fluoride (HF), hydrogen chloride (HCl) or the like and an~~
~~inert gas; a mixed gas containing an inert gas and an acid~~
~~such as nitric acid (NH_3) or sulfuric acid (H_2SO_4) or the~~
~~like; a mixed gas containing an inert gas and a gas~~
containing as a hydride of the component element of a thin
film of a semiconductor or the like, such as silane (SiH_4 ,
 Si_2H_6) as a representative. As the inert gas, nitrogen
(N_2), single rare gases such as helium (He), neon (Ne),
argon (Ar), krypton (Kr), xenon (Xe) and the like; mixed
gases containing these gases, all gases chemically inert
for thin films subjected to melt crystallization and mixed
gases containing these gases and the above inert gases can
be used.

~~Progress of~~ Melt crystallization of a thin film in an
atmosphere containing an inert gas and hydrogen has the
advantage^s that it is possible to significantly decrease
contamination of the thin film with impurities such as
oxygen and dust particles floating in air, and improve the
purity of the crystalline film formed, as compared with
crystallization in atmosphere. For semiconductor films
and metallic films, it is well known that as the amounts

of ~~the~~ impurities in the film decreases, ^{the} physical properties of the film such as mobility are improved. For semiconductor films, impurities are intentionally added in trace amounts of about $1 \times 10^{18} \text{ cm}^{-3}$ or less to control the physical properties of the films. From this viewpoint, ~~also~~, it is important to obtain a high-purity semiconductor film. Contamination of the thin films from air becomes more serious in melt crystallization than in crystallization (solid phase crystallization ^{or "SPC"}) in a solid state. This is because in a liquid state where the processing temperature is higher than that in solid phase crystallization, impurities diffuse and chemically react with the components of the thin films at higher rates. Therefore, control of the atmosphere in metal crystallization ^{is more critical} ~~has more important meaning~~ than in solid phase crystallization.

^{for reasons which follow} ~~discussed below~~
It is important from ~~the viewpoints below~~ that the atmosphere for progressing metal crystallization contains hydrogen. When a thin film is melted by supplying high energy and then solidified to a crystal, the adjacent atoms in the thin film combine with each other to form a regular crystal structure. However, on the ^{upper half of the} surface, no bonding atoms ^{are} ~~is present in the upper half thereof~~. Hence, in melt crystallization under vacuum or in an inert gas,

~~on the surface of the thin film~~, unpaired bonding
 electrons combine with each other to reconstruct the
 surface. ^{on the surface of the thin film.} The structure of the reconstructed surface is
^{significantly} ~~greatly~~ different from the inner structure of the crystal,
~~thereby~~ causing a change in the band structure. In
 addition, large stress is present in the reconstructed
 surface. This stress ^{causes} ~~affects~~ lattice distortion ^{which affects the} ~~the~~
^{surface} ~~crystal~~ ^{line film.} ~~positioned in an under layer up to several periods~~
~~thereof~~. A change in the band structure changes the
 concentrations of electrons and holes, and the lattice
 distortion decreases the mobilities ^{is} ~~ies~~ of electrons and
 holes. In addition, bonding of atoms on the surface
~~invariably~~ produces unpaired bonding electrons. These
 electrons are chemically active and thus react with water
 and oxygen in ^{the} ~~air~~ ^{and also} ~~or~~ absorb dust when the thin film is
 exposed to air at the end of ^{the} ~~crystallization~~ ^{process.} ~~of the thin~~
~~film~~. In addition, the presence of unpaired bonding
 electrons produces interfacial levels and scattering
 centers of electrons and holes, thereby deteriorating ~~the~~
 mobilities ^{is} ~~ies~~ of electrons and holes. Therefore, the
 reconstructed surface ~~has various~~ ^{ly} ~~adverse~~ ^{effects} ~~on~~ the
 physical properties of the thin films.

In the method of forming a crystalline film of the
~~present~~ invention, melt crystallization of the thin film

proceeds in an atmosphere containing hydrogen. Therefore, the unpaired bonding electrons ~~of atoms~~ which appear on ^{thin film} the surface ^{during} in the cooling solidification process are terminated by various types of hydrogen atoms (~~abbreviated~~ ^{herein after} to "hydrogen termination") ~~hereinafter~~ contained in the atmosphere. The reconstruction of the surface is thus avoided, and at the same time, the total number of ~~the~~ unpaired bonding electrons is significantly decreased.

Therefore, ~~namely~~, the crystalline film obtained in accordance with the ~~present~~ invention has high purity and a surface structure extremely close to the inner crystal ^{line} structure. As a result, the metallic surface simply reflects the intrinsic physical properties possessed by a metal itself, and the semiconductor surface also ~~honestly~~ exhibits the physical properties of the semiconductor. For example, when a FET (so-called TFT) ^{including} ~~comprising~~ a polycrystal semiconductor thin film is formed according to the present invention, ^{because the} ~~since~~ mobility hardly deteriorates due to the reconstructed surface, the effective mobility is significantly improved, ~~as~~ compared ^{to} with the effective mobility of a TFT formed by ~~a~~ conventional technique^s, and ~~The value of mobility~~ ^{value} also does not change with substrates and lots.

~~In~~ ^M melt crystallization under ~~an~~ ⁱⁿ ~~atmosphere of a~~ ^{mixed gaseous}

~~mixed gas~~ containing hydrogen molecules and an inert gas,
 does ^{not introduce} ~~no~~ impurity is introduced into a crystallized film of a
 metal or semiconductor, and ^{therefore,} a high-purity crystallized
 film terminated with hydrogen is obtained. ^{During} ~~In~~ melt
 crystallization of a semiconductor film of silicon or ~~the~~
~~like~~ ^{an} under ~~a~~ atmosphere containing a hydrogen halide and
 an inert gas, the crystallized semiconductor film is
 securely terminated with hydrogen ^{because} ~~on the basis of the fact~~
 that the halide ^{relatively easily} reacts with the
 semiconductor film. This is particularly effective ^{for} ~~to a~~
 metallic thin film. It is ideal ^{for} ~~to progress~~ melt
 crystallization ^{to progress} ~~in an~~ ^{mixed gaseous} atmosphere of a ~~mixed gas~~ containing
 an inert gas and a gas containing a hydride of the
 component of the thin film. This is because hydrogen
 termination ^{occurs} ~~is securely performed~~, and high purity is
 guaranteed. ^{For example} ~~Particularly,~~ when the thin film ^{includes} ~~comprises~~
 silicon, the best hydride is silane. Since silane rapidly
 reacts, it ^{securely} reacts with the unpaired bonding
 electrons which appear on the surface. This ^{occurs} ~~is~~ because,
 as a result of reaction, even if silane is captured by the
 silicon thin film, only a silicon atomic layer is formed,
 without causing ~~neither~~ ^a decrease in purity ^{or} ~~and~~ nor lattice
 distortion.

In order to securely effect hydrogen termination in

melt crystallization, the ~~sufficient~~ ^{should be} partial pressure of hydrogen or hydride in the atmosphere ~~is~~ ^{is} about 10 mTorr or more. This is based on the following reasons. If the mass of one molecule of a gas is m (kg), the partial pressure is P (Pa), the temperature is T (K), the concentration is C (m^{-3}) and the average velocity is v ($m \cdot s^{-1}$), ^{then} the flux density F ($m^{-2} \cdot s^{-1}$) of the gas is ~~as~~ ^{represented by} the following equation:
~~follows~~

$$F = \frac{1}{6} \frac{1}{\sqrt{3kTm}} \dots (1) \text{ [Equation 1]}$$

wherein k is the Boltzmann's constant. If the melting time of recrystallization is indicated by τ (s), and the density of unpaired bonding electrons on the thin film surface is indicated by N_{ss} (m^{-2}), in order to terminate all unpaired bonding electrons, it is a necessary condition that the number of gas molecules (flux density \times melting time) which collide with the thin film surface within the melting time is larger than the density of unpaired bonding electrons. Namely, the following equation is established:

$$F \tau > N_{ss} \dots (2) \text{ [Equation 2]}$$

From Equations (1) and (2), the following equation is obtained for pressure:

$$2 \sqrt{3kTm}$$

$$P > \frac{Nss}{t \tau} \dots (3) \text{ [Equation 3]}$$

$$t \tau$$

When the partial pressure of hydrogen atoms or hydride satisfies Equation 3, a high quality surface can be obtained after melt crystallization. The ~~possible~~ ^{possible} shortest time of melt crystallization is generally 10 ns ($\tau = 1 \times 10^{-8}$ s), and the maximum density of the unpaired bonding electrons, ~~which is conceivable in a practical manner~~ is about $1 \times 10^{12} \text{ cm}^{-2}$ ($Nss = 1 \times 10^{16} \text{ cm}^{-2}$). Therefore, if the partial pressure of hydrogen molecules or hydride is ~~higher~~ ^{higher} than the pressure calculated ~~by~~ using these values, Equation (3) is satisfied in melt crystallization of all thin films. The minimum partial pressure calculated for each hydride is as follows:

hydrogen molecule (H_2)	$\text{PH}_2 > 1 \text{ mTorr}$
hydrofluoric acid (HF)	$\text{PHF} > 3 \text{ m Torr}$
hydrochloric acid (HCl)	$\text{PHCl} > 4 \text{ mTorr}$
silane (SiH_4)	$\text{PSiH}_4 > 4 \text{ mTorr}$
nitric acid (HNO_3)	$\text{PHNO}_3 > 6 \text{ mTorr}$
sulfuric acid (H_2SO_4)	$\text{PH}_2\text{SO}_4 > 7 \text{ mTorr}$

Equation (3) indicates that the minimum partial pressure of a hydride increases as the molecular weight increases. However, the above results ^{also} indicate that ~~also~~

~~all~~ almost all materials have a
 partial pressure ~~of~~ higher than about 10 mTorr. ~~almost all~~
~~materials satisfy the condition.~~ The ~~explosion~~ lower
 limit ^{of hydrogen} ~~concentration of hydrogen~~ is about 4%, and the
 partial press^{ure} of hydrogen corresponding to this value is
 about 30 Torr. From the viewpoint of safety, the maximum
 partial pressure of hydrogen is ~~said to be~~ about 30 Torr.
 The ~~explosion~~ lower limit ^{of silane} ~~concentration of silane~~ is
 about 1%, and the partial press^{ure} of silane corresponding
 to this value is about 7.6 Torr. From the viewpoint of
 safety, the other hydrides are preferably used at
 concentrations of about 1% or less, or partial pressure of
 about 7.6 Torr or less. With a margin for safety, the
 maximum partial pressure is ~~said to be~~ about 5 Torr.
 Therefore, Eventually, for all hydrides (including hydrogen
molecules), the partial pressure of melt crystallization
^{which} ~~for~~ ^{es} ~~safely achieving~~ ^{objed} ~~the~~ ^{of the} ~~present~~ invention is 10 mTorr to
 5 Torr.

Although the partial pressure of ^{the} hydride used in the
 second step has been described above, the total pressure
 is preferably atmospheric pressure or higher. Of course,
 melt crystallization under low pressure (vacuum) which
 satisfies the above partial pressure condition produces
 the same effect as described above. However, in a vacuum
 system apparatus, the cost is increased, and the process

complicated. Melt crystallization under atmospheric pressure simplifies the apparatus and the process, thereby significantly improving productivity. Further, when processing in the second step is carried out under atmospheric pressure or higher, in metal crystallization, it is possible to significantly decrease evaporation and scattering of the component elements of the thin films and adhesion of the evaporated and scattered elements in the apparatus, as compared with processing under vacuum

(~~hereinafter~~ referred to as "scattering suppression effect"

~~hereinafter~~). This is caused by the fact that the melted surface is pressed by the gases which form the atmosphere, and evaporation and scattering are suppressed in proportion to pressure. Since the degree of this effect is determined by the level of total pressure, in principle, even if the pressure of only the hydrogen molecules or hydride used is increased to atmospheric pressure without using an inert gas, the same scattering suppression effect as the use of a mixed gas containing a hydride and an inert gas under atmospheric pressure can, of course, be obtained. However, it is very dangerous to handle such hydrides under atmospheric pressure. For this reason (the of guarantee for safety), a mixed gas containing hydrogen or hydride and an inert gas is preferable. As advantage of low price. When a metal or semiconductor is

the inert gas, nitrogen is most widely used and has the advantage ^{being inexpensive} of low price. When a metal or semiconductor is put into a high-temperature liquid state by supplying high energy, it reacts with nitrogen. However, rare gases have the advantage that they ^{do not under any circumstances} ~~by no means~~ react with ~~any~~ ^{any} thin film materials, even at high temperatures. Materials ^{utilized} ~~for~~ thin films such as silicon and aluminum have relatively high atomic weights. Thus, of the rare gases, ^{elements with high} ~~weight~~ ^{atomic weights} elements, such as argon, krypton and xenon, have the larger scattering suppressing effect. Since ~~the abundances of~~ ^{are not found in abundance,} krypton and xenon ~~are low and~~ these elements are ~~thus~~ expensive. ^{However, argon gas is} ~~An inert gas which is~~ inexpensive, and practical and exhibits ^a ~~the~~ large scattering suppression effect. ~~is argon.~~

~~(1-2 Form of a high energy supply apparatus and metal crystallization by the apparatus)~~

→ ^{is required for} ~~In order to~~ ^{to} stably progress, the second step in which ~~there~~ ^{In the second step,} high energy is supplied to an object material, such as the semiconductor thin film and metallic thin film formed on the substrate in the first step ^{of the invention,} to melt and crystallize at least the surface layer, and ~~in order to~~ obtain a high-quality crystal, A high energy supply apparatus suitable for this purpose is required. ~~In this chapter, forms of~~

CAPS
→

Detailed Description of ~~the~~ PREFERRED EMBODIMENTS

The high energy supply apparatus ^{is} described ~~by~~ using light (laser beam) as an example of ^a ~~the~~ form of high energy, with reference to ^{Figure} ~~Fig.~~ 2. ~~At the same time,~~ The method of forming a crystalline film, using the thin film formed on the substrate in the first step ^{of the invention} as the object material to which high energy is supplied ^{during} in the second step, will be discussed. ^{shown} ~~illustrated~~ in Figure 2, ~~see page~~

The high energy supply apparatus ^{includes} ~~(Fig. 2)~~ of the ~~present invention comprises~~ at least a generation source (laser emission source) 202 for generating high energy 207 such as a laser beam, and a supply chamber 201 in which the generated high energy is supplied to an object material (the substrate on which a thin film is formed). The supply chamber ²⁰¹ has a function (setting base) 205 for setting the object material 203 in the supply chamber. The setting base ²⁰⁵ is provided with a movable function so that the high energy 207 can be supplied to a desired position of the object material. In a portion of the wall 209 of the supply chamber ²⁰¹ is provided an introduction window 206 for introducing high energy ²⁰⁷ into the supply chamber. ²⁰⁶ ^{includes} The introduction window ^{comprising} a material which ^{little} ~~less~~ absorbs ^{high} energy and ~~hardly~~ ^{few} transmits ^{gas} molecules. In other words, the introduction window ²⁰⁶ is transparent to high energy ²⁰⁷ and opaque to gas molecules.

For example, when the form of high energy is light, the introduction window ^{includes} comprises transparent glass such as quartz. ~~or the like.~~

In the ~~present~~ invention, the introduction window ²⁰⁶ is provided at a position where, when high energy is supplied to the object material ²⁰³ (for example, a silicon thin film), the components (in the case of a silicon thin film, silicon atoms) of the object material ²⁰³ hardly adhere to the introduction window. For example, in the high energy supply apparatus, ~~shown in Fig. 2,~~ a portion of the wall of the supply chamber ²⁰¹ is projected in a direction apart from the object material ²⁰³, and the introduction window ²⁰⁶ is provided at the top of the projected portion 210. As a result, the distance L1 between the introduction window ²⁰⁶ and the object material ²⁰³ is larger than the shortest distance L2 between the wall 209 and the object material. ²⁰³

In a state wherein the distance between the introduction window ²⁰⁶ and the thin film as the object material is larger than the shortest distance between the wall ²⁰⁹ and the thin film, i.e., in a state wherein the introduction window ²⁰⁶ is provided at a position where the components of the thin film hardly adhere to the introduction window ²⁰⁶ even by supplying high energy ²⁰⁷ to the thin film, the high energy 207 is supplied to the thin film as the object material. ²⁰³

In Fig. 2, the scattering range of the elements evaporated
 and scattered from the object material²⁰³ as a result of
 supply of high energy²⁰⁴ (irradiation of a laser beam) is
 shown as the scattered component. ~~It~~ In the ~~present~~
 invention, since the introduction window²⁰⁶ is sufficiently
 separated from the object material²⁰³, as compared with the
 scattering range of the object material²⁰³, the components of
 the object material²⁰³ hardly adhere to the introduction
 window²⁰⁶ even if melt crystallization by supplying high
 energy²⁰⁴ is repeated. As described above, the introduction
 window²⁰⁶ must be transparent to high energy. Since the
 object material²⁰³ is opaque to high energy, high energy is
 converted into heat. If the object material²⁰³ adheres to
 the introduction window²⁰⁶, the introduction window becomes
 opaque and thus does not have the function to fulfil. In
 the ~~present~~ invention, ~~such an unreasonableness is~~
~~rejected,~~ and ^a the high energy supply apparatus having
 excellent stability and productivity is realized.

When a crystallized film is obtained by irradiating
 the semiconductor thin film with a laser beam, it is
 particularly important to control the scattering range.
 Generally, the higher the energy supplied to the
 semiconductor thin film ~~is~~, the ~~more~~ ^{er} easily a good
 crystallized film is obtained. However, if the supplied

energy exceeds a certain upper limit, the semiconductor elements are explosively scattered, resulting in the absence of the semiconductor thin film or a decrease in the thickness thereof after supply of high energy. This is possibly caused by the fact that the semiconductor film ~~comprises~~^{includes} a covalent^{ly} bond^{ed} crystal and is hard^{er} and has lower thermal conductivity than that of metals. Another possible cause is that since the semiconductor thin film is deposited by the vapor phase deposition process (CVD process) in the first step, the adhesion between the semiconductor film and the substrate or a surface protective film formed on the substrate is low.^{It} In either case, since the upper limit is present, the energy of the laser beam supplied for performing crystallization is set to as a high value as possible, which is lower than the upper limit. However, the energy of the laser beam invariably changes, and ~~the~~^{it} explosive scattering occurs in a statistical process. Therefore, in order to obtain a good crystalline semiconductor film, the scattering phenomenon cannot necessarily be ignored. From the above situation, it can be concluded that the high energy supply apparatus and the crystallized film forming method of the present invention, in which the scattering range is controlled, are particularly suitable for stably forming a

good crystalline semiconductor film on the substrate or the surface protective film with high productivity.

In order to decrease the size of the high energy supply apparatus ~~itself~~ and facilitate replacement of the atmosphere in the supply chamber, the unnecessary space in the supply chamber must be eliminated as much as possible. In consideration of setting and removal of the object material²⁰³ and vibration in ^{the} operation of the setting base²⁰⁵, the shortest distance between the wall and the object material²⁰³ is ~~about~~ ^{approximately} 2 mm to 40 mm. On the other hand, the scattering range of the object material²⁰³ changes with pressure in the supply chamber. For example, the scattering range under a vacuum of about 10^{-5} Torr reaches ^{approximately} about 10 cm or more, while the scattering range under atmospheric pressure is ^{approximately} ~~about~~ 10 mm or less. Therefore, if melt crystallization is progressed under pressure of atmospheric pressure or higher, as described above, ~~in the previous chapter,~~ the sufficient distance between the introduction window²⁰⁶ and the object material²⁰³ is about 20 mm or more. If high energy²⁰⁷ is supplied under pressure of about 10 mTorr or less, the distance is preferably at least about 50 mm, and ideally 100 mm or more. From these viewpoints, in order to comply with various pressures in the supply chamber²⁰¹, the distance is preferably about 50 mm

or more. Although there is no upper limit of this distance, if the upper limit is positively set, the upper limit is about 1000 mm. If the distance is too long, the volume of the supply chamber is increased, ^{a lot of} much time is required for replacing the atmosphere, and the size of the apparatus itself is also increased.

~~(1-3. Gas flows in the high energy supply apparatus and melt crystallization performed thereby)~~

~~In the previous chapter,~~ ^{The} ~~The optimum form of the high energy supply apparatus has been described.~~ ^{is} ~~In this~~ ^{above} ~~chapter,~~ ^{The} gas flows in the supply chamber of the high energy supply apparatus will be described with reference ^{Figure} to Fig. 3.

Fig. 3(A) shows the structure of the supply chamber of the high energy supply apparatus described in the previous chapter from the viewpoint of the gas flows, and Fig. 3(B) shows gas flows ³²⁰ in the middle of crystallization of the object material performed by at least supplying high energy to the object material (the thin film formed on the substrate). The high energy supply apparatus of the ~~present~~ ^{includes} invention ~~comprises~~ pressure regulating means for generating a desired pressure distribution in the supply chamber 301, or gas flow regulating means for

generating desired gas flows in the supply chamber.³⁰¹
Specifically,^{referring to Figure 3(A),} the pressure regulating means or the gas
flow regulating means ^{includes} ~~comprises~~ at least an exhaust port
311 and a gas inflow port 312. The exhaust port is
provided at a portion of the wall 309 of the supply
chamber, for exhausting the air in the supply chamber. A
plurality of gas inflow ports (at the 6 positions shown in
Fig. 3(A)) are provided for flowing the various gases
described in detail ^{earlier} ~~in Chapter (1-1)~~ in the supply
chamber. The amount of the gas flowing through each of
the gas inflow ports and the exhaust rate of the exhaust
port are appropriately adjusted to control the total
pressure and flows in the supply chamber by the pressure
regulating means and the gas flow regulating means.

§ Additionally
Besides, the pressure regulating means and the gas flow
regulating means are capable of increasing the pressure in
the vicinity of the introduction window 306 to a value
higher than that in the vicinity of the object material,
and increasing the pressure in the vicinity of the object
material to a value higher than that in the vicinity of
the exhaust port. Therefore, in the second step, the high
energy ³⁰³ 307 is supplied to the object material³⁰³ such as the
thin film set on the setting base 305 in the state wherein
the pressure in the vicinity of the introduction window is

higher than that in the vicinity of the object material³⁰³, or the pressure in the vicinity of the introduction window 306 is higher than that in the vicinity of the object material 303 (thin film) and the pressure in the vicinity of the object material³⁰³ (thin film) is higher than that in the vicinity of the exhaust port.

The gas flows in this state will be described with reference to Fig. 3(B). First, the path of the high energy which is introduced into the supply chamber 301 through the introduction window 306 and then applied to the object material 303 is assumed in the supply chamber.

Part of the high energy which reaches the object material through the irradiation passage enters the object material, and another part thereof is scattered and reflected from the object material. In this application, at Figure 3(A) the scattered reflected high energy is referred to as "reflected energy"³¹³. The path of the reflected energy 313 in the supply chamber is assumed as a reflection passage ^{as shown in Figure 3B.} 314. As described above, the pressure distribution and gas flows 320 regulated by the pressure regulating means and the gas flow regulating means, respectively, are present in the supply chamber³⁰¹. In the supply chamber³⁰¹ of the high energy supply apparatus of the ~~present~~ invention, the gas flows³²⁰ can be controlled so that gases flow toward

the object material from the introduction window in substantially the same direction as the irradiation passage, ³¹⁵ and flow from the object material in substantially the same direction as the reflection passage. ³¹⁴ ^{occurs because} This ~~is caused by the fact that~~ the pressure in the vicinity ~~317~~ of the introduction window ³¹⁷ is higher than that in the vicinity ~~318~~ of the object material, ³¹⁸ and the pressure in the vicinity of the object material is higher than that in the vicinity ~~319~~ of the exhaust port. ³¹⁹

Eventually, high energy is supplied to the object material such as the thin film to progress melt crystallization in the state wherein the gases flow from the introduction window in substantially the same direction as the irradiation passage and flow from the object material in substantially the same direction as the reflection passage.

^{above}
~~As described in the previous chapter,~~ ^{by} in melt crystallization of a metal or semiconductor, the component elements of the metal or semiconductor are invariably evaporated. With supply of high energy, the component elements are scattered as a fine powder. In the high energy supply apparatus of the ~~present~~ invention, since ~~the~~ gas flow from the introduction window side to the object side is present, the probability that the

evaporated elements or scattered fine powder reach the introduction window is significantly decreased. Since ~~the~~ gas flow³¹⁰ from the object material to the exhaust port^{is present} in substantially the same direction as the reflection passage ~~is also present~~, the evaporated elements or scattered fine powder are exhausted through the gas flow. This ~~fact~~ not only prevents adhesion to and contamination of the supply chamber but also significantly restricts re-adhesion of the evaporated elements or scattered fine powder to the object material. ~~Particularly,~~ ^{particularly,} This^{has} has an important meaning when a TFT or a super integrated circuit (LSI) is manufactured by using ~~the~~ crystallized thin film formed on the substrate. This is because the fine powder which re^{ad}heres to the thin film causes deterioration ~~in~~ of precision ~~of fine~~ processing and ^{results in} electrical short circuits. Since the fine powder is chemically active and has high reactivity to the wall of the supply chamber, the fine powder possibly re-adheres to the object material such as the thin film after such chemical reaction, thereby deteriorating the purity of the thin film itself. The high energy supply apparatus and the crystalline film forming method of the present invention can completely remove these adverse effects, and stably produce a good crystal.

~~(1-4. Utilization of reflected energy)~~

~~In this chapter,~~ ^{earlier} The high energy supply apparatus of the ~~present~~ invention described in detail in Chapter (1-2) ^{described as is} is further improved and a method of forming a crystalline film using the apparatus, ~~will be described.~~

Fig. 4 shows the structure of a supply chamber 401 of the high energy supply apparatus of the ~~present~~ invention. ~~As described in Chapter (1-2),~~ The high energy supply apparatus ^{includes} ~~comprises~~ at least a generation source ~~(omitted in Fig. 4)~~ for generating high energy 407 and a supply chamber ⁴⁰¹ for supplying high energy ⁴⁰⁷ to an object material 403 (a metallic thin film or a semiconductor thin film).

In the supply chamber, ⁴⁰³ is provided setting means 405 having the function to set the object material ^{supply} in the chamber ⁴⁰¹.

The object material ^{403,} ^{of the invention} as a substrate having a thin film formed in the first step, ^{is} being set on the setting means.

In a portion of the wall 409 of the supply chamber ⁴⁰¹ is ^{is provided} ~~provided~~ an introduction window for introducing high

energy ⁴⁰⁷ into the supply chamber ⁴⁰¹ so that the positional relationship between the introduction window 406 and the object material ⁴⁰³ satisfies the conditions described in ^{condition above} ~~Chapter (1-2).~~

~~Chapter (1-2).~~ In the supply chamber ⁴⁰¹ ~~are provided~~ pressure regulating means and gas flow regulating means ^{are provided} ~~which include~~ comprising an exhaust port 411 and gas inflow ports 312,

respectively, so that the pressure distribution and gas flows described ^{earlier} ~~in Chapter (1-3)~~ are present in the supply chamber ⁴⁰¹. Of course, the atmosphere in the supply chamber ⁴⁰¹ is set according to the description ^{discussed earlier.} ~~in Chapter (1-1)~~. The path of the high energy ⁴⁰⁷ introduced into the supply chamber ⁴⁰¹ through the introduction window ⁴⁰⁶ and then applied to the object material ⁴⁰³ is ~~assumed as~~ the irradiation passage ⁴¹⁵.

In the high energy supply apparatus of the ~~present~~ invention, the introduction window ⁴⁰⁶ or the setting means ⁴⁰⁵ is disposed so that ^{the direction of 416 line} the normal ⁴⁰³ of the object material ⁴⁰³ such as the thin film is shifted from the direction of the irradiation passage 415. Therefore, in crystallization of the thin film, high energy ⁴⁰⁷ is supplied to the thin film in the state wherein the normal direction ^{416 of the normal line} of the thin film is deviated from the direction of the irradiation passage ⁴¹⁵.

In the high energy supply apparatus of the ~~present~~ invention, an exhaust port ⁴¹¹ is also provided in the normal direction ⁴¹⁶ of the object material such as the thin film. Such a configuration permits an increase in the distance between the introduction window ⁴⁰⁶ and the object material ⁴⁰³ in the small supply chamber ⁴⁰¹, and easily produces the same construction and effect described in Chapter (1-2). In addition, since the exhaust port ⁴¹¹ is provided at a position ⁴⁰³ at the shortest distance between the object material ⁴⁰³ and

the wall of the supply chamber,⁴⁰¹ the evaporated elements and scattered fine powder are effectively discharged. Further, since the rate of discharge of the evaporated elements and scattered fine powder in the normal direction⁴¹⁶ ~~of the normal line~~ is particularly high, the efficiency of discharge is improved, and the effect described ~~in Chapter~~ ^{earlier} (1-3) is securely attained.

The high energy supply apparatus of the ~~present~~ ^{also includes} invention ~~further comprises~~ means for changing the course of reflected energy so that the object material⁴⁰³ is irradiated again with the reflected energy 413. The course changing means 418 ~~further comprises~~ ^{includes} positioning means for permitting a desired position of the object material⁴⁰³ such as the thin film to be irradiated with the reflected energy.⁴¹³ After the thin film formed on the substrate in the first step is set in the supply chamber,⁴⁰¹ a first position of the thin film is irradiated with high energy.⁴⁰⁷ Part of the high energy⁴⁰⁷ enters the thin film, and another part is reflected from the thin film to generate reflected energy.⁴¹³ The course of the reflected energy⁴¹³ is changed by the course changing means so that a second position of the thin film is again irradiated to progress melt crystallization. If the high energy⁴⁰⁷ has a high velocity, as light, irradiation of the second position is

generally started with the reflected energy corresponding to the high energy for irradiating the first position of the thin film during the time of irradiation of the first position of the thin film with the high energy. The first position and the second position are adjusted by the positioning means. ⁴¹⁷ If the high energy ⁴⁰⁷ is light, the course changing means comprises an optical device such as a mirror, a lens or a prism. If the high energy is charged particles, the course changing means comprises an electromagnetic generator. The positioning function ⁴¹⁷ is the function to change the positional relation (for example, the angle of the mirror) of an optical device, or finely adjust an electromagnetic field.

~~Figure~~
~~Fig. 5~~ shows ~~an example of~~ the simplest apparatus using light as high energy, ^{where} ~~Reference numeral 506 denotes~~ ^{is} an introduction window, ~~reference numeral 511~~ ^{is} an exhaust port, ~~reference numeral 512~~ ^{is} a gas inflow port, and ~~reference numeral 516~~ ^{is} a normal line. ~~In this example,~~ Course changing means 518 ^{includes} ~~comprises~~ a mirror, preferably converging means such as a concave mirror, ~~or the like~~. Although reflected light generally contains scattered components, the converging means converges scattered light to permit efficient re-irradiation. Incident light is applied to the object material ⁵⁰³ ~~305~~ such as the thin film

and is then partially reflected to generate reflected light⁵¹³. The reflected light⁵⁷³ is converged and reflected by the concave mirror, and then applied to the object material⁵⁰³ again. This can significantly increase the efficiency of utilization of the high energy 507. For example, reflectance of ultraviolet light and visible light by a semiconductor thin film reaches about 70% or more, and the reflectance by a metal thin film is about 90% or more. Although a convention^{al} efficiency of energy utilization is ~~about~~ ^{approximately} 10% to 30%, the ~~present~~ invention can substantially double the efficiency of energy utilization from ~~about~~ ^{approximately} 20% to 50% because the reflected energy 513 is efficiency re-utilized. This is particularly remarkable when the irradiation position (first position) where the object material is irradiated with high energy is substantially the same as the irradiation position (second position) where the object material is irradiated with the reflected energy. ~~In Fig. 6,~~ This effect is described with reference to an example in which a laser beam is emitted as pulses. ^{and is illustrated in Figure 6} In Fig. 6, the time at the non-irradiation point of the object material is shown on the abscissa, and irradiation is started at $t = 0$. The intensity of energy (arbitrary unit) which actually enters the object material to contribute to melt crystallization

axis
is shown on the ordinate. When irradiation is started, the energy intensity of the high energy is increased to the maximum at $t = t_1$. The reflected energy is applied to the object material with a slight delay corresponding to the distance between the object material and the course changing means and the velocity. It is assumed that the time the energy density of the reflected energy is the maximum is t_2 , the delay is indicated by $t_2 - t_1$. In this way, the energy density of the incident high energy is superimposed on the energy density of the reflected energy. ~~In this application.~~ This total of energy density actually contributes to melt crystallization. ~~Figure~~ ~~Fig~~ 6 shows this effect as synthetic light. As described above, the ~~present~~ invention can substantially double the conventional efficiency of energy utilization.

In the ~~further improved~~ high energy supply apparatus of the ~~present~~ invention, the course changing means has the function ^{of} ~~to~~ adjusting time. This function ~~is to~~ delays the time (shown by $t_2 - t_1$ in Fig. 6) of re-irradiation of the object material with the reflected energy. (~~In this application, the delay is referred to as "the delay time"~~ ^{hereinafter} ~~hereinafter~~). For example, the time regulating means 419 ^{in Figure} 4 can be composed of a plurality of reflecting means which can reflect the high energy. ~~Figure~~ ~~Fig~~ 4 shows a simple

example of this means. If the high energy is light, the reflecting means is composed of combination of mirrors. The time regulating means⁴¹⁹ is means for changing the length of the course of the reflected energy⁴¹³ or changing the velocity of the reflected energy⁴¹³. The former means is useful when the high energy is light, and the latter means is useful when the high energy is charged particles. This is because the course length of light can be changed by changing combination of mirrors, and the velocity of charged particles can be changed by adjusting an electric field. The irradiation time of the object material with high energy can be increased by appropriately adjusting the delay time. This will be described below with reference to ^{Figure} Fig. 7. ~~Fig.~~ In Fig. 7, the same things as those shown in Fig. 6 are respectively shown on the abscissa and the ordinate. In Fig. 7, the delay time ($t_2 - t_1$) is substantially the same as the emission time width (the half width of incident light shown by t_a in Fig. 7) of the high energy. As a result, the half width of the synthetic light is substantially doubled (shown by t_b in Fig. 7).

An increase in the time half width of the high energy means that energy is rapidly supplied to the object material, and the probability of occurrence of the explosive scattering can significantly be decreased. For

example, the hydrogenated amorphous silicon film (a-Si:H) formed by a plasma chemical vapor phase deposition process (PECVD process) is used as the object material, and the object material is crystallized by irradiation with a xenon-chlorine (XeCl) excimer laser (abbreviated to a XeCl laser with a wavelength of 308 nm) as high energy. This thin film generally has a high hydrogen content and a low density, and is thus very difficult to melt crystallize. In fact, an amorphous film is not at all crystallized by a XeCl laser having a time half width of about 50 ns with an irradiation energy density of about $100 \text{ mJ}\cdot\text{cm}^{-2}$ or less. Conversely, if the energy density exceeds this value, explosive scattering occurs. Eventually, the thin film is not crystallized over the entire energy region. On the other hand, the amorphous thin film is not crystallized by a XeCl laser having a time half width of about 100 ns with an irradiation energy density of about $100 \text{ mJ}\cdot\text{cm}^{-2}$ or less, while with an energy density between about $100 \text{ mJ}\cdot\text{cm}^{-2}$ to $150 \text{ mJ}\cdot\text{cm}^{-2}$, melt crystallization completely proceeds. Although, with an energy density of about $150 \text{ mJ}\cdot\text{cm}^{-2}$ or more, the explosive scattering occurs as described above, the energy density range which enables melt crystallization is widened by further increasing the time half width. Even with the same energy density of 125

$\text{mJ}\cdot\text{cm}^{-2}$, high energy having a short time half width (50 ns) and high energy having a long time half width (100 ns) have different effects on the object material. This difference is based on a difference in the energy transfer per unit time. With a long time half width, the amount of the energy transferred from high energy to the object material per unit time is decreased, thereby suppressing the explosive scattering. This is the same as a difference between combustion and explosion of an explosive. Explosion means the phenomenon which occurs when the energy transfer per unit time is large. For this ^{ese} reasons, in melt crystallization of an amorphous semiconductor film formed by PECVD or sputtering process at a relative low temperature (the substrate temperature is about 400°C or less) by supplying high energy, the time half width of the high energy is preferably about 100 ns or more. As described above, ~~in the present invention~~, it is possible to simply increase the time half width, and crystallize the thin film which was conventionally considered as difficult to melt crystallize.

~~(1-5. Method of manufacturing thin film electronic device)~~

The high energy supply apparatus described in detail ~~in the above chapters~~, and the crystalline film formed by

using the apparatus can be applied to various thin film electronic devices, ^{including} ~~such as~~ semiconductor devices such as TFTs and LSIs, metal-insulator-metal elements (MIM elements), solar cells, printed boards, etc., and the performance thereof can significantly be improved. In ^A ~~this chapter, the~~ method of manufacturing an excellent thin film electronic device with reference to a TFT with highest applicability as an example, ^{is described.}

^{Figures A - D}
Figs. 8 (a) ~~to (d)~~ are schematic sectional views showing the steps of manufacturing a thin film semiconductor device (so-called TFT) which constitutes a MIS type field effect transistor. The method of manufacturing a TFT in accordance with the ~~present~~ invention will be briefly described.

The ~~present~~ invention uses general purpose non-alkali glass as ^{sample} ~~an example of the~~ substrate. ^{In Figure 8(A),} On a substrate 801 ^{is formed / then including} ~~is formed~~ a surface protective film 802 comprising an insulator by an atmospheric pressure chemical vapor deposition process (APCVD process), ^a the PECVD process or ^{or the like} the sputtering process. A semiconductor film, such as an intrinsic silicon film serving as an active layer of a thin film semiconductor device, ^{as the} is then deposited ^{as the} ~~first~~ first step for the semiconductor film. The semiconductor film is formed by a chemical vapor deposition process (CVD

process) such as PECVD, APCVD or LPCVD or a physical vapor phase deposition process (PVD process), such as sputtering or vapor deposition. The ~~thus obtained~~ semiconductor film is supplied with high energy, such as a laser beam ^{for example,} ~~as a~~ ^{for the} ~~representative~~ to progress melt crystallization ~~to~~ second step for the semiconductor film. If the thin film deposited in the first step is amorphous or a mixed crystal containing an amorphous material and a fine crystal, ^{the} ~~this~~ second step is generally called "the crystallization step". On the other hand, if the thin film deposited in the first step is polycrystalline, ^{the second} ~~this~~ step is called the recrystallization step. ~~In the specification of this application,~~ No distinction is made between both cases, and this step is simply called the "crystallization step." Both cases correspond to the melt crystallization of this application as long as at least the surface of the thin film is melt crystallized by supplying high energy. ~~§~~ Melt crystallization is an ~~extremely~~ excellent technique from the viewpoint that a high quality crystalline thin film can be formed on a large substrate with high productivity. In melt crystallization, by supplying high energy, the energy supply time (with a laser beam, the irradiation time) is generally as short as about 10 ns to 500 ns, and the

energy supply region (laser irradiation region) is localized on the entire substrate. Thus, in crystallization, the entire substrate is not simultaneously heated to a high temperature, thereby causing no deformation ~~and~~^{or} cracks due to the heat of the substrate. After the crystalline semiconductor film (polycrystalline silicon film) is formed according to the crystalline film forming method described ~~in detail~~ above, the crystalline semiconductor film is processed to an island form, and an active semiconductor film 803 serving as an active layer of a transistor is formed ~~(Fig. 8(a))~~.

After the active semiconductor film is formed, a gate insulating film 804 is formed by CVD or PVD (Fig. 8(b)).
Referring to Figure 8(c),
A metallic thin film serving as a gate electrode 805 is then deposited by PVD or CVD. Since the gate electrode and gate wiring are generally formed by using the same material in the same step, the material used must have low electric resistance and resist the highest temperature (in this example, about 350°C) and chemicals in the subsequent steps for manufacturing the thin film electronic device. Thus, a tantalum (Ta) film having such properties is formed by sputtering ~~(a first step for the metal)~~. The tantalum thin film formed by sputtering generally has a β -structure and resistivity of as high as about 200 $\mu\Omega\text{cm}$.

The tantalum thin film also has internal stress and is apt to cause disconnection when used for wiring. In the ~~present~~ invention, therefore, high energy is supplied to the tantalum thin film (a second step for the metal) to improve the quality of the thin film. When melt crystallization of the tantalum metallic thin film is progressed by the method described ^{earlier} ~~in detail in the~~ ~~previous chapters~~, the crystallized film comprises α -structure tantalum (Ta). The α -structure tantalum has a cubic crystal system and a body-centered cubic crystal structure (bcc). The α -structure tantalum also has a resistivity of about 20 $\mu\Omega\text{cm}$ to about 60 $\mu\Omega\text{cm}$ and low internal stress. The α -structure tantalum is ^{an} ~~extremely~~ excellent ~~as a~~ wiring material, as compared with the above β -structure tantalum.

After the metallic thin film ^{which serves,} ~~serving~~ as the gate electrode and gate wiring is formed, shaping is carried out. Then, impurity ions are injected into the active semiconductor film to source-drain regions and ~~a~~ channel formation region 806, 807 and 808, ^{as illustrated in figure 8(c).} ~~(Fig. 8(c))~~. At this time, since the gate electrode is used as a mask for ion injection, the channel formation region is formed only under the gate electrode in a self alignment manner. In order to inject impurity ions, ^{methods can be used:} ~~two types including an~~ ^{an}

doping method for injecting hydride and hydrogen as impurity elements ~~to be~~ injected by using a mass non-separation ion injection apparatus; and an ion implantation method for injecting only a desired impurity element by using a mass separation type ion injection apparatus, ~~can be used.~~ When ^aCMOS TFT is formed, an appropriate mask material, such as polyimide resin, ~~or the like~~ is used, and NMOS and PMOS are alternately masked to inject each ion by using one of the ~~above methods~~ ^{described}. Referring to Figure 8(D), ~~then~~ ^{then}, a layer insulating film 809 is formed by CVD or PVD. After ion injection and formation of the layer insulating film, heat treatment is carried out for several ~~tens~~ ^{between} minutes to several hours in an appropriate heat environment of about 350°C ^{or less} to activate the injected ions and thermally shrink the layer insulating film. After the layer insulating film is formed, contact holes are formed above the source and drain, and a source-drain lead-out electrode 810 and wiring 811 are formed. At this time, the melt crystallization of the metallic thin film described ^{earlier} ~~in the previous chapters~~ may be applied to the metal which constitute the source-drain electrodes and wiring, as the gate electrode and gate wiring. After the crystalline metallic film is formed, the thin film is processed to electrodes and wiring to complete a thin film

semiconductor device (Fig. 8(d)).

~~(2-1. Substrate and surface protective film to which the present invention is applied)~~

~~In this chapter,~~ The substrate and the surface protective film ^{is now described below.} ~~to which the present invention is applied will be described. As the~~ ^{materials} Substrate ^{include} to which the present invention can be applied, conductive materials such as metals, ceramic materials such as silicon carbide (SiC), alumina (Al₂O₃), ^{and} aluminum nitride (AlN), ~~and the like;~~ transparent insulating materials, such as fused quartz, ~~and glass and the like;~~ semiconductor substrates ^{including} ~~such as~~ silicon wafers; and crystalline insulating materials, such as LSI obtained by processing semiconductor substrates, ~~and sapphire (trigonal system Al₂O₃ crystal), and the like can be used.~~ ^{example of inexpensive} ~~As an~~ ^{low price} general purpose glass substrate, #7059 glass or #1737 glass produced by Corning Japan Co., Ltd., or OA-2 glass produced by Nippon Denki Glass Co., Ltd., ^{or} NA35 glass produced by NH Technoglass Co., Ltd. ~~and the like~~ can be used. [#] When a thin film semiconductor device is manufactured by using a crystalline semiconductor thin film, or when metallic wiring is formed by using a crystalline metallic thin film, at least a part of the substrate comprises an insulating material, and the

crystalline thin film is formed on the insulating material regardless of the type of the substrate used. ~~In this application,~~ ^{hereinafter} The insulating material film is referred to as "the surface protective film". For example, when a fused quartz substrate is used, since the substrate itself ~~comprises~~ ^{includes} an insulating material, a crystalline film may be formed directly on the fused quartz substrate.

Alternatively, the crystalline thin film may be formed after an insulating material such as a silicon oxide film (SiO_x : $0 < x \leq 2$) or a silicon nitride film (Si_3N_x : $0 < x \leq 4$) is formed as the surface protective film on the fused quartz substrate. [#] When a glass plate is used as the

substrate, generally, a crystalline film such as a semiconductor film may be formed directly on the glass substrate ~~comprising~~ ^{including} an insulating material. However, in order to prevent contamination of the thin film with

movable ions such as sodium (Na) contained in glass, the crystalline film is preferably formed after the surface protective film is formed on the glass substrate by using an insulating material such as silicon oxide or silicon

nitride. The thin film electronic device, such as the thin film semiconductor device manufactured as described ^{earlier} above

~~causes~~ ^{has} no variation in operational characteristics in use for a long time or under a high voltage, thereby improving

stability. In the case of the crystalline semiconductor film, the thin film is preferably formed on the surface protective film, except the case where a crystalline insulating material such as sapphire is used as the substrate. When any one of various ceramic substrates is used as the substrate, the surface protective film is preferably provided for preventing a sintering auxiliary material added to ceramic from diffusing into the thin film and contaminating it. When a metallic material is used as the substrate, the surface protective film is necessary and essential to secure insulating properties. In addition, in a semiconductor substrate and LSI device, the layer insulating film or the like provided between transistors or wiring layers plays a part as the surface protective film. The size and shape of the substrate are not at all limited as long as no deformation such as shrinkage, distortion or the like occurs in the heat environment of the manufacturing process. Namely, any desired substrate including a disk having a diameter of 3 inches *76.2 mm) and a rectangular substrate of about 600 mm x 800 mm or more can be used.

~~(2-2. Thin films to which the present invention can be applied, and gases containing the components thereof)~~

~~In this chapter,~~ The thin films to which the ~~present~~ invention is applied, and gases containing the component elements of semiconductor films among the gases which constitute the atmospheres ^{earlier are} described ~~in Chapter (1-1)~~ will be described ~~below~~.

In the ~~present~~ invention, any kinds of crystalline materials can be used as the object material. For example, the ~~present~~ invention can be applied to melt crystallization of diamond. ~~Or the like.~~ However, when a semiconductor thin film or a metallic thin film is selected as the object material, the advantageous effects of the ~~present~~ invention ^{are} is most simply ^{and} securely exhibited. The ~~present~~ invention ^{also} can be applied to all types of metals. Particularly, the ~~present~~ invention is effective for materials such as tantalum ^{, described earlier} ~~described in~~ Chapter (1-5) wherein the crystal phase is changed by supplying high energy or melt crystallization. Other metals in which the crystal grain size is increased as a result of metal crystallization are also preferred. Semiconductor thin films are most suitable for application of the ~~present~~ invention, ^{because} because the semiconductor thin film formed in the first step is amorphous or crystalline with low quality, but ~~such~~ a low quality thin film is easily improved to an excellent crystalline thin film by

carrying out the second step of the ~~present~~ invention.

The types of semiconductor films to which the ~~present~~ invention can be applied include single semiconductor films of silicon (Si) ^{and} germanium (Ge) ~~and the like~~; semiconductor films of Group IV element composite materials such as silicon*germanium ($\text{Si}_x\text{Ge}_{1-x}$: $0 < x < 1$), silicon*carbide ($\text{Si}_x\text{C}_{1-x}$: $0 < x < 1$), ^{and} germanium*carbide ($\text{Ge}_x\text{C}_{1-x}$: $0 < x < 1$); ~~and the like~~; semiconductor thin films of composite compounds of Group III elements and Group V elements such as gallium*arsenic (GaAs), ^{and} indium*antimony (InSb); ^{and} ~~and the like~~ thin films of composite compounds of Group II elements and Group VI elements such as cadmium*selenium (CdSe), ~~and the like~~. The ~~present~~ invention can also be applied to semiconductor thin films of composite compounds such as silicon*germanium*gallium*arsenic ($\text{Si}_x\text{Ge}_y\text{Ga}_z\text{As}_z$: $x + y + z = 1$); N type semiconductor films obtained by adding a donor element, such as phosphorus (P), ^{or} arsenic (As), antimony (Sb) ~~or the like~~ to these semiconductor films; and P-type semiconductor films obtained by adding an acceptor element such as boron (B), aluminum (Al), gallium (Ga), indium (In) ~~or the like~~ to these semiconductor films.

When the semiconductor film ^{includes} ~~comprises~~ silicon (Si),

gases containing the component element of the semiconductor film include silanes, such as monosilane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), ^{and} dichlorosilane (SiH_2Cl_2) ~~and the like~~. When the semiconductor film ~~comprises~~ ^{includes} germanium, germane (GeH_4) is used. When the semiconductor film ~~comprises~~ ^{includes} phosphorus (P) or boron (B), or when such an element is added to an intrinsic semiconductor film, phosphine (PH_3) ~~and~~ ^{or} diborane (B_2H_6) ~~and the like~~ can also be used. Although chemical materials containing the elements which ~~constitute~~ ^{include} the above various semiconductor films are used as gases for forming the atmosphere, ^{because} ~~since~~ these gases ~~necessarily~~ partially remain in the semiconductor films, hydrides of the component elements are preferably used. For example, chlorine (Cl) ~~variably~~ remains in a silicon film formed by using dichlorosilane (SiH_2Cl_2), regardless of the amount of chlorine, and thus residual chlorine causes deterioration in transistor characteristics when the silicon film is used for the active layer of a thin film semiconductor device. Therefore, monosilane (SiH_4), which is a hydride of the component element, is preferred ~~as~~ as compared with dichlorosilane.

~~(2-3. Laser beam as high energy)~~

~~In this chapter,~~ ^{sources,} Types of light ^a when a laser beam is
^{source is described below.} used as high energy ^{will be described.} The laser beam
 used in the ~~present~~ invention is not limited, and various
 light sources are used ^{in accordance with} ~~according to~~ the object material
 used. A KrF excimer laser (wavelength 248 nm) and a XeCl
 excimer laser (wavelength 308 nm) are widely used in the
 industrial field because of stable emission of light.
~~Also,~~ ^{Also,} Besides, a ArF excimer laser and a XeF excimer laser
 (wavelength 351 nm) can also be used as the excimer ^{laser} ~~layer~~.
 A YAG laser, a carbon dioxide laser, a Ar main beam laser
 (wavelength 514.5 nm), a Ar sub-beam laser (wavelength 448
 nm), a HeNe laser (wavelength 632.8 nm), a HeCd laser
 (wavelength 441.6 nm), and other various pigment lasers
 can also be used. When the object material is a
 semiconductor film ^{which includes} ~~comprising~~ silicon as a main component,
^{an} a XeF laser, ~~the~~ Ar main beam laser, Ar sub-beam laser, HeNe
 laser, and HeCd laser exhibit higher absorption
 coefficients in the amorphous component than that in the
 crystalline component. This means that in a system
 containing an amorphous component and a crystalline
 component, energy absorption of the amorphous component is
 higher than that of the crystalline component, and the
 temperature of the amorphous component easily rises.
 Namely, crystallization of the amorphous component more

easily takes place than recrystallization of the crystalline component. ~~As~~ ^{for example,} described above, in melt crystallization of the semiconductor film, as the energy supplied increases within the range which causes no damage to the semiconductor film, the quality of the crystallized film obtained is improved. If the temperature of the crystalline component more easily rises, the semiconductor film is damaged before the amorphous component is completely crystallized. In other words, the film is damaged before recrystallization is completed. The XeF laser ~~or the like~~ ^{damage to the film} does not ~~causes such a trouble~~ ^{is}, and ~~can~~ ^{therefore} thus be said to be very suitable for melt crystallization of a silicon semiconductor film. It is ~~thus~~ ^{therefore} important to select ~~the~~ ^a high energy source ~~so that the~~ ^{whereby the} absorption coefficient of the object material before supply of high energy is higher than that of the crystalline object material after supply of high energy.

Since the KrF laser and XeC laser exhibit high absorption coefficients in a semiconductor film ~~comprising~~ ^{including} silicon as a main component, these lasers are suitable for crystallization of thin films having a thickness of ~~about~~ ^{approximately} 50 nm or less. The absorption coefficients of the XeF laser and HeCd laser are slightly lower than those of the KrF laser and XeCl laser, and thus the XeF laser and HeCd

laser are suitable for crystallizing silicon semiconductor thin films having a thickness of about 50 nm to 1000 nm. Since the absorption coefficients of Ar main beam laser and Ar sub-beam layer and HeNe laser in semiconductor films are low, they are suitable for crystallizing semiconductor thin films having a thickness of about 1000 nm or more.

As described above, the ~~present~~ invention enables simple stable melt crystallization of the object material by supplying high energy thereto, and easy formation of high-quality crystalline films. Such crystalline thin films permit manufacture of excellent thin film electronic devices. Specifically, the ~~present~~ invention has the following effects:

~~Effect~~ (1) Since crystallization ^{progresses} ~~is progressed~~ under control of an atmosphere which can ~~easily~~ safely be replaced; ^{no impurities} ~~no impurity~~ such as oxygen, nitrogen or dust ~~is~~ are captured by the crystalline thin film. Particularly, when the crystalline film ^{includes} ~~comprises~~ a semiconductor or metal, high purity and high quality crystalline film can be obtained.

~~Effect~~ (2) It is possible to supply high energy under atmospheric pressure, and thus simplify the high energy supply apparatus. ^{This} decreases the cost of a thin film

electronic device ^{which includes} ~~comprising~~ the crystalline film, and increases productivity;

~~Effect~~ (3) In melt crystallization, the component elements of the object material are necessarily scattered or evaporated from the melted object material. It is possible to protect the incident window from evaporation, and thus keep the high energy supplied to the object material constant. A crystalline film having good characteristics can thus be obtained, and the quality of the film is significantly stabilized.

~~Effect~~ (4) ^{As} ~~In progress of~~ melt crystallization ^{progresses} by supplying high energy, such as laser irradiation, to the object material, ^{and} as the energy supplied increases, the quality of the resultant crystal is generally improved. ~~In this application,~~ Since high energy can be applied under atmospheric pressure, even if the supplied energy is increased, ~~the~~ phenomenon such as scattering or evaporation can be suppressed, thereby improving the quality of the crystalline film.

~~Effect~~ (5) Control of the surface plays an important role in obtaining a good crystalline film. In the crystallization method of the ~~present~~ invention, the control of the surface is sufficiently achieved, and thus an excellent crystalline film can be obtained. Further,

since the recrystallized surface is controlled to the same state ^{for} ~~in each time of~~ melt crystallization, the film characteristics ~~of the crystalline film~~ are significantly stabilized.

~~Effect~~ (6) The efficiency of use of high energy can be substantially doubled. In addition, the time half width can be increased, and a material which cannot be crystallized by a conventional process can be crystallized.

Brief Description of the Drawings

Fig. 1 ~~is a drawing~~ ^{shows} a conventional laser irradiation apparatus; # Fig. 2 ~~is a drawing~~ ^{shows} a high energy supply apparatus ^{according to an embodiment} of the present invention; # Fig. 3 ~~is a drawing~~ ^{shows} a high energy supply apparatus of the present invention; # Fig. 4 ~~is a drawing~~ ^{shows} a high energy supply apparatus ^{according to an embodiment} of the present invention; # Fig. 5 ~~is a drawing~~ ^{shows} a high energy supply apparatus of the present invention; # Fig. 6 is a ^{chart} drawing showing changes in the high energy supplied to an object material with time; # Fig. 7 is a ^{chart} drawing showing changes in the high energy supplied to an object material with time; # Figs. 8(A) to (D) are sectional views showing ~~a device~~ in the respective steps for manufacturing a thin film semiconductor device

These and other aspects and advantages of the invention will become apparent from the following detailed description of preferred embodiments when taken in conjunction with the accompanying drawings, in which

Move to after page

in accordance with an embodiment of the ~~present~~ invention;

~~Figure~~ ^{shows}

~~Fig. 9 is a drawing showing~~ the configuration of a

transmission type liquid crystal display device according

to the ~~present~~ invention; # ~~Figure~~ ^{is a flowchart}

~~Fig. 10 is a drawing showing~~ the configuration of an electronic apparatus according to

the ~~present~~ invention; ~~Figure~~ ^{shows a} ~~Fig. 11 is a drawing showing an~~

~~example~~ ^{utilizing an} liquid crystal projector ~~an~~ electronic apparatus

according to the ~~present~~ invention; ~~Figure~~ ^{shows} ~~Fig. 12 is a drawing~~

~~showing another example~~ ^{an} (personal computer) of ^{an} electronic

apparatus ~~according to the present invention;~~ ~~Figure~~ ^{is} ~~Fig. 13 is~~

~~a drawing showing~~ ^{shows} a further example (pager) of ^{an} electronic

apparatus ^{utilizing} according to the ~~present~~ invention.

~~Best Mode for Carrying out the Invention~~

~~The present invention will be in further detail below with reference to the drawings.~~

~~(Embodiment 1)~~

~~In another embodiment of the invention,~~

A ~~surface protective film~~ ^{includes} comprising a silicon oxide

film ~~is~~ formed on a large glass substrate of 360 mm x 475

mm x 1.1 mm by the PECVD process, and an intrinsic silicon

film ^{is} ~~is~~ then formed on the surface protective film without

breakage of ^{the} vacuum. ^{This is} ~~the first step for silicon~~ ^{deposition}.

The thickness of the surface protective film is 300 nm, and

the thickness of the semiconductor film is 60 nm. The

glass substrate in equilibrium with room temperature is set in an PECVD apparatus in which a lower plate electrode is kept at a temperature of 380°C. Conditions for depositing the silicon film are as follows:

Time: $t = 164 \text{ s}$

Flow rate of silane: $\text{SiH}_4 = 100 \text{ SCCM}$

Flow rate of argon : $\text{Ar} = 3000 \text{ SCCM}$ (raw material concentration 3.23%)

Power of radio frequency: $\text{RF} = 600 \text{ W}$ (0.228 W/cm^2)

Pressure: $P = 1.5 \text{ Torr}$

Electrode distance: $S = 37.1 \text{ mm}$

Temperature of the under plate electrode: $T_{\text{sus}} = 380^\circ\text{C}$.

Temperature of the substrate^{is} surface: $T_{\text{sub}} = 349^\circ\text{C}$

The deposition rate of the semiconductor film under these conditions was 0.365 nm/s , and the thickness of the semiconductor film was 60 nm . The hydrogen concentration of the silicon film which was measured by thermal desorption gas spectroscopy (TDS) was 10.39 atomic \% .

Observation by a transmission electron microscope indicated~~ed~~ that the silicon film mainly ~~comprises~~^{includes} a mixed crystal containing a prismatic structure amorphous component. The results of Raman spectroscopic measurement of the silicon film show~~ed~~^{ed} a Raman shift at about 520 cm^{-1} ,

and thus indicates^d that the silicon film of the ~~present~~
invention ~~comprises~~^{includes} a mixed crystal.

The ~~thus obtained~~^{then} silicon film was irradiated with a laser beam to progress melt crystallization,³ the second step for silicon³. Melt crystallization is carried out by a high energy supply apparatus having the laser irradiation chamber (supply chamber) shown in ~~Fig.~~^{Figure} 4. The laser beam is irradiated by using a KrF excimer laser having a wavelength of 248 nm and a half width of about 33 ns. Since reflected light is applied again with a delay time of about 30 ns by the time regulating means, the substantial time half width is about 60 ns. The time regulating means ~~comprises~~^{includes} a combination of mirrors, and the total length of the optical path of the reflected light is about 9 m. Incident light is applied at an angle of 60° with respect to the normal line. Since the shortest distance between the thin film and the wall of the supply chamber is 20 nm, the distance between the introduction window and the irradiation position on the thin film is generally 40 nm. The laser beam has a linear shape having a width of 120 μm and a length of 38 cm. The widthwise overlap of the beams applied in respective irradiations is 90% of the width of a beam. Therefore, a beam advances by 12 μm in each irradiation, and the same

point on the semiconductor thin film is irradiated with a laser beam ten times. The energy density of the laser beam is $150 \text{ mJ} \cdot \text{cm}^{-2}$. Irradiation of the laser beam is performed under atmospheric pressure. Mixed gases containing argon and monosilane are introduced into the supply chamber at a rate of 1 slm through the gas inflow port, and discharged through the exhaust port provided on the normal line of the thin film. The gases flow from the introduction window and the course changing means, including the positioning function and the time regulating means, to the irradiation position, and further ^{continues} ~~flow~~ from the irradiation position toward the exhaust port. Since the silane concentration of argon is generally 100 ppm, the partial pressure of silane is generally about 76 mTorr in irradiation with the laser beam. In irradiation with the laser beam, the substrate ^{at} temperature is room temperature of about 25°C . The degree of crystallization of the ~~thus~~ crystallized semiconductor film, which was measured by multiwavelength dispersion type epsometry, was 98%, and the thickness ~~thereof~~ was 55 nm. Raman spectroscopic measurement shows a sharp peak with a half width of 4.4 cm^{-1} at about 515 cm^{-1} which indicates a Raman shift caused by the crystalline component. This indicates that a high quality film having high

crystallinity is formed. After the crystallization step, this crystalline film is patterned, and an active layer semiconductor film serving as an active layer of a transistor is then formed.

A gate insulating film is then formed by PECVD. The gate insulating film ~~comprising~~^{including} a silicon oxide film is deposited to a thickness of 100 nm at a substrate surface temperature of 350°C by using TEOS ($\text{Si}-(\text{O}-\text{CH}_2-\text{CH}_3)_4$), oxygen (O_2) and water (H_2O) as raw material gases and argon as a dilution gas. After the gate insulating film is formed, the oxide film is heat-treated in an atmosphere containing oxygen at a partial pressure of about 0.2 atm and water vapor with a dew point of about 80°C at a temperature of about 350°C for about 3 hours to improve the quality of the insulating film.

A tantalum (Ta) thin film serving as a gate electrode is then deposited by sputtering (the first step for tantalum). In sputtering, the substrate temperature is 150°C, and the thickness of the film is 500 nm. The ~~thus~~
~~obtained~~ tantalum film is then irradiated with a laser (the second step for tantalum). Conditions for laser irradiation are the same as the conditions for crystallization of the semiconductor film except that the atmosphere gas is changed to mixed gases containing argon

and hydrogen. Since the hydrogen concentration of argon is about 1%, the partial pressure of hydrogen in laser irradiation is generally 7.6 Torr. The tantalum film after laser irradiation has the α structure, as described ^{earlier} above, and a resistivity of about $40 \mu\Omega\text{cm}$. After the tantalum thin film ^{is formed} as the gate electrode, ~~is formed~~ pattering is performed.

An impurity ion is then injected into the semiconductor film to form source-drain regions and a channel region. At this time, the gate electrode served as a mask for injection, and the channel is formed only under the gate electrode in the self alignment manner. In this example, TFT having a CMOS structure is formed. The PMOS TFT portion is covered with a polyimide resin in formation of NMOS TFT source-drain, and conversely the NMOS TFT portion is covered with a polyimide resin in formation of PMOS TFT source-drain to form the CMOS TFT. An impurity ion is injected by using a mass non-separation type ion injection apparatus, and about 5% of phosphine (PH_3) diluted with hydrogen is used as a raw material gas for HMOS. The total of the ions including PH_3^+ and H_2^+ implanted is $1 \times 10^{16} \text{ cm}^{-2}$, and the concentration of phosphorus atoms in the source-drain regions is about $3 \times 10^{20} \text{ cm}^{-2}$. In ion injection, the substrate temperature is

250°C. For PMOS TFT, about 5% of diborane (B_2H_6) diluted with hydrogen is used as a raw material gas. The total of the ions including $B_2H_6^+$ and H_2^+ implanted is $1 \times 10^{16} \text{ cm}^{-2}$, and the concentration of boron atoms in the source-drain regions is about $3 \times 10^{20} \text{ cm}^{-2}$. In ion injection, the substrate temperature is also 250°C.

A layer insulating film ~~comprising~~^{including} a silicon oxide film is then formed by the PECVD process using TEOS. In deposition of the layer insulating film, the surface temperature of the substrate is 350°C, and the thickness of the film is 500 nm. Then heat treatment is performed at 350°C in an oxygen atmosphere for 1 hour to activate the injected ions and thermally shrink the layer insulating film. Contact holes are then formed on the source-drain, and aluminum (Al) is deposited by sputtering. In sputtering, the substrate temperature is 150°C, and the thickness of the Al film is 500 nm. The aluminum thin film for forming a source-drain lead out electrode and wiring is patterned to complete a thin film semiconductor device.

The transistor characteristics of the thin film semiconductor device formed on an experimental base were measured. The source-drain current I_{ds} when the transistor is turned on at a source-drain voltage V_{ds} of

± 4 V and a gate voltage V_{gs} of ± 10 V is defined as an on current I_{ON} (+ and - signs of voltage indicate the measurement conditions of NMOS and PMOS, respectively). The source-drain current I_{ds} when the transistor is turned off at V_{ds} of ± 4 V and V_{gs} of 0 V is defined as an off current. Measurement was carried out for a transistor in a channel formation region having a length L of 5 μm and a width W of 5 μm at a temperature of 25°C. Mobility and threshold voltage were calculated from the saturation current. In this embodiment, in order to examine the performance of the transistor and variations in the substrate thereof, measurement was made for 50 transistors uniformly formed on a large glass substrate. The results obtained are as follows:

NMOS TFT

$$I_{ON} = (74.3 + 9.0, -6.8) \times 10^{-6} \text{ A}$$

$$I_{OFF} = (1.38 + 0.53, -0.37) \times 10^{-12} \text{ A}$$

$$\mu = 124.1 \pm 12.6 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$$

$$V_{th} = 2.13 \pm 0.13 \text{ V}$$

PMOS TFT

$$I_{ON} = (51.6 + 4.7, -4.1) \times 10^{-6} \text{ A}$$

$$I_{OFF} = (3.87 + 0.99, -0.80) \times 10^{-13} \text{ A}$$

$$\mu = 69.3 \pm 6.04 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$$

$$V_{th} = -1.11 \pm 0.11 \text{ V}$$

Therefore, the ~~present~~ invention is capable of uniformly manufacturing an excellent CMOS thin film semiconductor device with high mobility on a large general-purpose glass substrate at ^a ~~the~~ highest temperature (350°C) ^{which is} ~~of the process as~~ the same ^{temperature} as a conventional a-Si TFT. Since the TFT obtained in this example ^{includes} ~~comprises the~~ a good crystalline semiconductor film and gate electrode, ^{its} the reliability as a transistor is extremely high, and ~~the~~ ^{its} operation is stable over a long period of time. In a conventional low-temperature process, uniformity of laser crystallization is a very important problem regardless of the substrates and lots. However, the ~~present~~ invention can significantly decrease variations in the on-current and off-current. This significant improvement in uniformity means that the crystalline silicon film of the ~~present~~ invention has excellent properties, and crystallization is stably progressed by the laser irradiation apparatus (high energy supply apparatus) used. In addition, since the tantalum film has low stress and low resistivity, when the thin film semiconductor device of the ~~present~~ invention is applied to LCD, uniform image quality can be obtained over the entire LCD screen. Further, when a circuit is formed by using the thin film semiconductor device of the ~~present~~ invention, not only

simple circuits such as a shift register and an analog switch but also complicated circuits such as a level shifter, a digital analog converter circuit, a clock generator circuit, a γ - correction circuit, and a timing controller circuit can easily be formed.

~~(Embodiment 2)~~

In another embodiment of the invention,
An active matrix substrate containing the NMOS thin film semiconductor device described above
~~obtained in Embodiment 1~~ and used as a color LCD pixel switching element comprising 200 (line) x 320 (column) x 3 (color) = 192000 (pixels), the CMOS thin film semiconductor device obtained *as described above*
~~in Embodiment 1~~ and used as a 6-bit digital data driver (column measurement driver) and a scanning driver (line measurement driver) was manufactured. The digital driver of this embodiment *includes*
~~comprises~~ a clock signal line, a clock generator circuit, a shift register circuit, a NOR gate, a digital image signal line, a latch circuit 1, a latch pulse line, a latch circuit 2, a reset line 1, an AND gate, a standard potential line, a reset line 2, a 6-bit D/A converter based on volume division, a CMOS analog switch, a common potential line, and a source line reset transistor, the output from the CMOS analog switch being connected to the source line of the pixel portion. The volume of the D/A converter satisfies the relation of $C_0 =$

$C_1/2 = C_2/4 = C_3/8 = C_4/16 = C_5/32$. ~~The~~ ^The digital image signal line is directly input to the digital image signal output from a video random access memory (VRAM) of a computer. In the pixel portion of the active matrix substrate of this embodiment, the source electrode and source wiring, drain electrode (pixel electrode) ~~comprise~~ ^{includes} aluminum to form a reflection type LCD. A liquid crystal panel ~~comprising~~ ^{including} the ~~thus formed~~ active matrix substrate as one of a pair of substrates is manufactured. A polymer dispersion liquid crystal (PDLC) in which a black pigment is dispersed is used as a liquid crystal held between the pair of substrates to form a reflection type liquid crystal panel in a normally black mode (a black display when no voltage is applied to the liquid crystal). The ~~thus obtained~~ liquid crystal panel is connected to external wiring to produce a liquid crystal display device. As a result, the NMOS and PMOS have substantially the same on resistance and transistor capacity, TFT has high performance, and the parasitic capacity of the transistor is very low. Further, since characteristics are uniform over the entire surface of the substrates, the 6-bit digital data driver and the scanning driver are normally operated over a wide operation range. Since the pixel portion has a high degree of opening, even if black

pigment dispersion PDLCD is used, a high quality liquid crystal display device can be obtained. Further, since the manufacturing process of the active matrix substrate is stable, the liquid crystal display device can stably manufactured at low cost.

This liquid crystal display device is contained in a casing of a full-color portable personal computer ~~(note PC)~~. The active matrix substrate contains the 6-bit digital data driver, and a digital video signal is input directly into the liquid crystal display device from the computer, the circuit configuration is simplified, and at the same time, power consumption is significantly decreased. Since the liquid crystal thin film semiconductor device has high performance, the ~~note~~ PC is a good electronic apparatus having a ^{clear} ~~very beauty~~ display screen. In addition, on the basis of the fact that the liquid crystal display device is a reflection type having a high degree of opening, a back light is made unnecessary, thereby realizing decreases in the size and weight of a battery and long-term use. As a result, a very small lightweight electronic apparatus which can be used for a long time and which has a ~~beauty~~ display screen could be formed.

Although an example using the reflection type active

matrix substrate had been described above, an embodiment of the ~~present~~ invention can be applied to a liquid crystal display device ~~comprising~~ ^{including} a transmission type active matrix substrate. ~~Fig. 9~~ ^{Figure} 9 shows the entire configuration of an example of such ^a liquid crystal display device. Namely, a liquid crystal display device ~~comprises~~ ^{includes} a back light 900, a polarizing plate 901, an active matrix substrate 903 provided with a driving circuit 902, a liquid crystal 904, a counter substrate 905 and a polarizing plate 906.

As illustrated in Figure 10, ^{including} an electronic apparatus ~~comprising~~ ^{includes} the liquid crystal display device of this embodiment ~~comprises~~ ^{includes} a display information output source 1000, a display information processing circuit 1002, a display driving circuit 1004, a display panel 1006 such as a liquid crystal panel, a clock generator circuit 1008 and a power source circuit 1010. The display information output source 1000 ~~comprises~~ ^{includes} memory such as ROM and RAM, and a tuning circuit for tuning a television signal and outputting it so as to output display information such as a video signal on the basis of the clock generated from the clock generator circuit 1008. The display information processing circuit 1002 outputs display information on the basis of the clock generated from the clock generator circuit 1008, The

display information processing circuit 1002 ^{includes} ~~comprises~~, for example, an amplification-polarity inversion circuit, a phase development circuit, a rotation circuit, a gammer correction circuit or clamp circuit. The display driving circuit 1004 ^{includes} ~~comprises~~ a scanning-side driving circuit and a data-side driving circuit to drive the liquid crystal panel 1006 to display an image. The power source circuit 1010 supplies electric power to each of the above circuits.

Examples of electronic apparatus having the above-described configuration include the liquid crystal projector, ^{Figure} shown in Fig. 11, a personal computer (PC) for multimedia and an engineering work station (EWS) shown in ^{Figure} Fig. 12, the pager shown in ^{Figure} ~~Fig.~~ 13, a portable telephone, a word processor, a television, a view finder type or monitor direct-viewing type video tape recorder, an electronic notebook, a table electronic computer, a car navigation device, ^{and} POS terminal, a device with a touch panel. ~~and the like.~~

The liquid crystal projector shown in Fig. 11 is a projection type projector ^{which includes} ~~comprising~~ a transmission type liquid crystal panel as a light valve, for example, employs a three-plate prism optical system.

In the projector 1100 shown in ^{Figure} Fig. 21, the

projection light emitted from a white light source lamp unit 1102 is divided into the three primary colors R, G and B by a plurality of mirrors 1106 and two dichroic mirrors 1108 in a light guide 1104, and the three light parts are guided to three liquid crystal panels 1110R, 1110G and 1110B for respectively displaying images of the three colors. The light parts modulated by the liquid crystal panels 1110R, 1110G and 1110B are respectively incident on the dichroic prism 1112 in three directions. In the dichroic prism 1112, red light R and blue light B are bent at 90°, and green light straight travels to form an image of each color. As a result, a color image is projected on a screen through a projection lens 1114.

The personal computer 1200// ^{Figure} shown in Fig. 12 ~~includes~~ ^{includes} comprises a body part 1204 having a key board 1202, and a liquid crystal display screen 1206.

The pager ~~shown~~ ^{Figure} 1300 in ~~Fig. 13~~ ^{includes} ~~comprises~~ a liquid crystal display substrate 1304, a liquid guide 1306 with a back light 1306a, a circuit substrate 1308, first and second shield plates 1310 and 1312, two elastic conductors 1313 and 1316, and a film carrier tape 1318, all of which are provided in a metallic frame. The two elastic conductors 1314 and 1316 and the film carrier tape 1318 are adapted for connecting the liquid crystal display

substrate 1304 and the circuit substrate 1308.

In this apparatus, the liquid crystal display substrate 1304 ~~comprises~~ ^{includes} a liquid crystal held between two transparent substrates 1304a and 1304b to form at least a dot matrix type liquid crystal display panel. On one of the transparent substrates can be formed the driving circuit 1004 shown in Fig. 10 or the driving circuit 1004 and the display information processing circuit 1002. Circuits which are not provided on the liquid crystal display substrate 1304 can be provided as external circuits of the liquid crystal display substrate on the circuit substrate 1308 shown in ~~Fig.~~ ^{Figure} 13.

~~Fig.~~ ^{Figure} 13 shows the configuration of the pager, and thus the circuit substrate 1308 other ~~than~~ ^{than} the liquid crystal display substrate 1304 is required. However, when a liquid crystal display device is used as a component of an electronic apparatus and when a display driving circuit is mounted on a transparent substrate, the minimum unit of the liquid crystal display device is the liquid crystal display substrate 1304. Alternatively, the liquid crystal display substrate 1304 fixed to the metallic frame 1302 serving as a casing can also be used as a liquid crystal display device as a component of an electronic apparatus. Further, in the case of a back light type, the liquid

crystal display substrate 1304 and the light guide 1306 provided with the back light 1306a can be contained in the metallic frame 1302 to form a liquid crystal display device.

The ~~present~~ invention is not limited to the above embodiments, and various modifications can be made within the scope of the ~~gist~~ of the invention. For example, the ~~present~~ invention can be applied to not only the above-described various liquid crystal panels but also electroluminescence, plasma display devices.

~~Industrial Applicability~~

As described above, ~~The~~ high energy supply apparatus of the ~~present~~ invention is ^{also} capable of stably producing high-quality crystallized films. The ~~thus obtained~~ crystalline films can be applied to thin film electronic apparatus such as thin film semiconductor devices, and significantly improve the performance thereof. The ~~present~~ invention can thus produce a thin film semiconductor device with high performance by using a low temperature process in which, for example, a low-price glass substrate can be used. When the ~~present~~ invention is applied to manufacture of an active matrix liquid crystal display device, a high quality large liquid

crystal display device can easily and stably be manufactured. Further, when the ~~present~~ invention is applied to manufacture of an electronic circuit, a high quality electronic circuit can easily stably be manufactured.

The thin film semiconductor device of the ~~present~~ invention is low priced and has high performance, and is thus optimum as an active matrix substrate of an active matrix liquid crystal display device. Particularly, the thin film semiconductor device is optimum as an active matrix containing a driver required to have high performance.

A liquid crystal display device to which the ~~present~~ invention is applied is low priced and has high performance, and is thus optimum as various displays including a full-color note PC.

The thin film electronic apparatus of the ~~present~~ invention is ^{*inexpensive*} ~~low priced~~ and has high performance, and ~~will~~,
Can be thus widely used for general purposes.

ABSTRACT

is

The ~~present~~ invention ~~discloses~~ a high energy supply apparatus for stably producing a high quality melt crystallized film, and a method of forming a crystalline film ~~is shown~~. Melt crystallization is performed under control^{led} ~~of the~~ reconstruction of the surface of the crystallized film, without contaminating the high energy supply apparatus. In addition, ~~the efficiency of~~ ^{is efficiently utilized through} utilization of high energy ~~is increased by reuse of~~ reflected energy.